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UNITED STATES PATENT APPLICATION

of

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for

NICKEL BARRIER END TERMINATION AND METHOD

## BACKGROUND OF THE INVENTION

The present invention relates to nonlinear resistive devices, such as varistors, and more particularly to methods of making such devices using controllable plating techniques in which the exposed end terminals of the device are plated with nickel barrier terminations while the exposed semiconductor body remains unplated.

Nonlinear resistive devices are known in the art, and are described, for example, in U.S. Patent 5,115,221 issued to Cowman on May 19, 1992, and is incorporated by reference.

With reference to the prior art shown in Figure 1, a typical device 10 may include plural layers 12 of semiconductor material with electrically conductive electrodes 14 between adjacent layers. A portion of each electrode 14 is exposed in a terminal region 16 so that electrical contact may be made therewith. The electrodes 14 may be exposed at one or both of opposing terminal regions, and typically the electrodes are exposed at alternating terminal regions 16 as illustrated. The exposed portions of the electrodes 14 are contacted by electrically conductive end terminals 18 that cover the terminal regions 16.

While an apparently simple structure, the manufacture of such devices has proved complex. For example, the attachment of the end terminals 18 has proved to be a difficult problem in search of a simplified solution. Desirably, the terminal regions 16 may be plated with nickel and tin-lead metals to increase solderability and decrease solder leaching. The process parameters in plating nickel to zinc oxide semiconductor bodies

has proved particularly vexing and has required complex solutions.

One method of affixing the end terminals 18 is to use a conventional barrel plating method in which the entire device is immersed in a plating solution. However, the stacked layers are semiconductor material, such as zinc oxide, that may be conductive during the plating process so that the plating adheres to the entire surface of the device. Thus, in order to provide separate end terminals as shown in Figure 1, a portion of the plating must be mechanically removed after immersion, or covered before immersion with a temporary plating resist comprised of an organic substance insoluble to the plating solution. However, the removal of the plating or organic plating resist is an extra step in the manufacturing process, and may involve the use of toxic materials that further complicate the manufacturing process.

It has also been suggested that the metal forming the end terminals 18 be flame sprayed onto the device, with the other portions of the surface of the device being masked. Flame spraying is not suitable for many manufacturing processes because it is slow and includes the creation of a special mask, with the additional steps attendant therewith. See, for example, U.S. Patent 4,316,171 issued to Miyabayashi, et al. on February 16, 1982.

It is also known to react a semiconductor body, having electrically conductive metal end terminations, with phosphoric

acid to selectively form a phosphate on the semiconductor body prior to providing end terminations using conventional barrel plating. See, U.S. Patent 5,614,074 issued to Ravindranathan on March 25, 1997.

As illustrated by the above known methods, a simplified manufacturing process for the attachment of the end terminals 18 has proved to be a illusive.

Accordingly, it is an object of the present invention to provide a novel method and device that obviates many of the prior art problems.

Accordingly, it is an object of the present invention to provide a novel method of manufacturing a semiconductor device by controllably reacting an exposed zinc oxide semiconductor device having an exposed end terminal region with a nickel plating solution to form a nickel barrier end termination over the semiconductor body end without plating the entire exposed semiconductor device.

It is another object of the present invention to provide a novel method of providing a semiconductor device by controllably partially immersing an exposed semiconductor body having a silver termination with a nickel plating solution while applying a biasing current to form a nickel barrier cap extending a selected distance up the exposed body of the semiconductor device.

It is yet another object of the present invention to provide a novel method of providing a semiconductor body with a nickel barrier cap without the use of a plating resist by positioning an

exposed end of the semiconductor body a selectable distance into a nickel plating solution for a controlled period.

It is still another object of the present invention to provide a novel method of providing metal termination of an exposed semiconductor body by contacting an end of the semiconductor body with an absorbent material impregnated with a nickel plating solution.

It is a further object of the present invention to provide a novel semiconductor device having naturally formed nickel terminations over a body of resistive plates interleaved between zinc oxide layers.

It is yet a further object of the present invention to provide a novel method of directly nickel plating zinc oxide bodies having a preferred zinc oxide volume resistivity for the plating method selected.

It is still a further object of the present invention to provide a novel method of manufacturing zinc oxide semiconductor devices minimizing solder leaching by providing a platinum-free and palladium-free silver termination and thereupon forming a nickel barrier termination.

These and many other objects and advantages of the present invention will be readily apparent to one skilled in the art to which the invention pertains from a perusal of the claims, the appended drawings, and the following detailed description of the preferred embodiments.

### BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a pictorial depiction of a prior art varistor.

Figure 2 is a vertical cross section of an embodiment of the device of the present invention.

Figure 3 is a vertical cross section of another embodiment of the device of the present invention.

### DESCRIPTION OF PREFERRED EMBODIMENTS

With reference now to Figure 2, an embodiment of a nonlinear resistive element 20 may include a body 22 having stacked zinc oxide semiconductor layers 24 with generally planar electrodes 26 between adjacent pairs of layers 24. The zinc oxide layers 24 need not be comprised of pure zinc oxide and may be comprised of a ceramic consisting principally of zinc oxide. Each electrode 26 may have a contactable portion 28 that is exposed for electrical connection to nickel barrier end terminations 30 that cover terminal regions 32 of the body 22 and contact the electrodes 26. The exterior portion of body 22 not covered with the end terminations 30 remain as exposed zinc oxide surface 38. Nickel barrier end terminations 30 may be plated with layers 34 of electrically conductive, solderable tin or tin-lead metal that form electrically contactable solderable end portions for the resistive element 20.

With further reference to Figure 3, in another embodiment of a nonlinear resistive manufactured using the method of the

present invention, element 20 includes body 22 having stacked zinc oxide semiconductor layers 24 and generally planar electrodes 26 between adjacent pairs of layers 24. Each electrode 26 may have a contactable portion 28 exposed for electrical connection to a first electrically conductive metal (preferably silver, platinum-free silver, or palladium-free silver) end terminations 36 with nickel barrier end terminations 30 thereupon, covering terminal regions 32 and extending a desired distance along body 22. As with the embodiment illustrated by Figure 2, nickel barrier end terminations 30 may be plated with layers 34 of solderable tin or tin-lead metal that form final electrically contactable end portions for the resistive element 20.

By way of example, in one embodiment the zinc oxide layers 24 may have the following composition in mole percent: 94-98% zinc oxide and 2-6% of one or more of the following additives; bismuth oxide, cobalt oxide, manganese oxide, nickel oxide, antimony oxide, boric oxide, chromium oxide, silicon oxide, aluminum nitrate, and other equivalents.

In a first embodiment of the method of the present invention, body 22 may be provided conventionally, electrodes 26 having contactable portions 28 exposed for electrical connection at terminal regions 32 with the remaining portions of body 22 being exposed zinc oxide surface 38. Process parameter control to avoid process boundary problems including: 1) plating not occurring, 2) plating not uniformly covering terminal regions 32,

3) plating too thick or thin; and 4) plating spread beyond the desired terminal region 32 onto exposed zinc oxide surface 38, requires the selection of nickel plating solution appropriate for an intended method of nickel barrier end termination plating--electro-plating, electroless plating, or brush plating.

Having determined the method of nickel plating, an end of body 22 controllable contacts the nickel plating solution to form a desirably thick nickel barrier end terminations 30 over terminal region 32. Complimentary parameter processes selection, identification of nickel plating solution, plating method, and controllable contact assures that nickel barrier end terminations 30 uniformly cover terminal region 32 without extending undesirably along exposed surface 38 and while avoiding unacceptable zinc oxide etching, which etching is known to cause electrical leakage currents and mechanical weakness in the final device.

With the appropriate parameter selection, the method of the present invention desirable allows the temperature of the nickel plating solution to remain uncontrolled such that the solution remains at approximately room temperature. The pH of the nickel plating solution may be maintained between 2 and 6. Contact between semiconductor body 22 and nickel plating solution may vary from 15 to 120 minutes to allow the formation of end termination 30 with a thickness between 1 and 3  $\mu\text{m}$ .

One embodiment of the present invention further includes forming solderable contact 34 over end termination 30 by



controllably immersing the nickel termination 30 into a room temperature solution containing one of Alkyl-tin, Alkyl-tin-lead, Tin-Lead sulfuric acid, or tin sulfuric acid having a pH from 2 to 6. The partial immersion may vary in the range from 10 to 120 minutes to allow the formation of solderable contact 34 with a cap thickness ranging from 3 to 6 um. Desirably, solderable contact plating may include application of a biasing current of approximately 0.3 to 2.0 A/dm<sup>2</sup>.

Another embodiment of the present invention is preferably suited to electroless and brush plating methods for forming nickel end terminations 30. For this embodiment, a nickel plating solution comprising a room temperature solution of nickel sulphate, dimethylamineborane, lactic acid, ammonium citrate, and ammonia may be used in combination with semiconductor body 22 having zinc oxide layers 24 with a resistivity in the range from 10<sup>10</sup> to 10<sup>12</sup> Ohms/cm. The pH of the nickel plating solution may be maintained between 2 and 6.

For electroless plating, one end of semiconductor body 22 is positioned a selectable distance into the nickel plating solution covering that end of body 22 and allowing the plating solution to travel up a portion of exposed zinc oxide surface 38.

Maintaining body 22 immersed for a period of 15 to 120 minutes provides for a nickel cap between 1 and 3 um.

For brush plating, a suitable absorbent material is impregnated with the nickel plating solution. One end of semiconductor body 22 is placed in contact with the impregnated

absorbent material such that terminal region 32 completely contacts the absorbent material. Pressure between body 22 and absorbent material is maintained to allow formation of nickel end termination 30 on terminal region 32 and a desired distance along exposed zinc surface 38. The contact period may vary between 15 and 120 minutes to control termination 30 thickness and travel up surface 38. Relative motion may be provided so that semiconductor body 22 moves relative to the absorbent material.

In another embodiment of the present invention, particularly suitable for electroplating, a first electrically conductive metal end termination 36 is provided intermediate end termination 30 and body 20 and further includes providing a nickel plating solution comprising one of nickel sulphate or nickel chloride, boric acid, a wetting agent, and a stress relieving agent with the plating solution maintained at a temperature of 50 to 70°C. First end termination 36 material may preferably comprise silver, platinum-free silver, and/or palladium-free silver and glass frit. The use of platinum-free and/or palladium-free silver reduces the cost of device manufacture. The silver/glass frit material may be conventionally applied onto opposing ends of body 20 and fired to mechanically bond the silver/glass frit materials to terminal regions 32 forming first end terminations 36. Firing temperatures of 550 to 800°C have provided favorable results.

Body 20 with first end termination 36 is partially immersed into the nickel plating solution for a period from 15 to 120

minutes while applying biasing current of 0.3 to 2.0 A/dm<sup>2</sup>. Variously controlling immersion depth, immersion time, and biasing current will control nickel barrier termination 30 thickness and travel upward along exposed zinc surface 38.

Optionally, a final solderable termination may be provided over nickel end termination 30 using a room temperature solution of one of Alkyl-tin, Alkyl-tin-lead, Tin-Lead sulfuric acid, or tin sulfuric acid. Solder plating solutions having a pH in the range of approximately 3 to 6 have been suitable when layers 34 are formed with an immersion period ranging from 10 to 120 minutes and a biasing current of 0.3 to 2.0 A/dm<sup>2</sup>. In the present invention, solder leaching is minimized without the use of more expensive platinum or palladium by coating first end termination 36 with nickel termination 30 so as to avoid silver leaching when the varistor device is soldered to a board.

While preferred embodiments of the present invention have been described, it is to be understood that the embodiments described are illustrative only and the scope of the invention is to be defined solely by the appended claims when accorded a full range of equivalence, many variations and modifications naturally occurring to those of skill in the art from a perusal hereof.

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